

Title	Long-lasting phosphorescence in Sn ²⁺ -Cu ²⁺ codoped silicate glass and its high-pressure treatment effect
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Long-lasting phosphorescence in Sn^{2+} – Cu^{2+} codoped silicate glass and its high-pressure treatment effect

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Long-lasting phosphorescence was observed at 510 nm in a Sn^{2+} – Cu^{2+} codoped Na_2O – CaO – SiO_2 glass at room temperature under UV illumination of 254 nm. When the glass was compressed under 3, 6, and 9 GPa, the phosphorescence shifted to 465 nm and its decay rate became shorter. The optical absorption spectra of the samples changed after compression, showing that the cupric ions were reduced to the cuprous ions. The high-pressure treatment also resulted in a lower-energy shift in the absorption edge. It was suggested that Sn^{2+} ions act as hole trapping centers, while oxygen vacancies surrounding by Ca^{2+} ions as well as active sites in the glass matrix, i.e., as electron trapping centers. © 2002 American Institute of Physics.
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Extreme processing such as high-pressure, high-temperature, and high magnetic field treatments will be useful methods in exploring new optoelectronic materials. In particular, glasses are promising in modifying their properties under such extreme conditions showing a variety of active and also specific optical and/or electrical properties, because the structure of glasses is expected to be more flexible than corresponding crystalline materials. So far, permanent densification phenomena have been reported for a number of oxide and chalcogenide glasses.^{1–4} High-pressure treatment of glass is of great interest from the viewpoint of glass science and technology, because the glass structure can be permanently modified and its optical, electrical, mechanical, and magnetic properties are greatly changed accordingly without changing the glass composition.

Silica-based materials are widely employed in the field of microelectronics and UV optics. In these materials, point defects play an important role since they can change chemical and physical properties of the materials. In general, such point defects result in undesirable degradation of electrical and/or optical properties, but they can also be used to exhibit some specific features or applications. A variety of metastable defects in glasses have been observed under extreme conditions. In particular, illumination of an excimer laser and a femtosecond laser induces a variety of metastable defects.^{5–7} It is hence likely that some novel optical func-

tions can be elicited if the characteristics and quantities of the defects can be controlled.

In this letter, we report the long-lasting phosphorescence phenomenon of Sn^{2+} - and Cu^{2+} -doped Na_2O – CaO – SiO_2 glass and the effect of pressure on the optical properties of the glass. The mechanism of the long-lasting phosphorescence phenomena is also discussed on the basis of the optical absorption and electron paramagnetic resonance (EPR) spectra of the glass samples before and after high-pressure treatment.

The composition of glass sample employed in this study is 70 SiO_2 ·20 Na_2O ·10 CaO ·0.05 CuO ·0.05 SnO in mol ratio. Details of the glass-preparation procedure have been described elsewhere.⁸ The high-pressure treatments were performed with a 6–8 multianvil high-pressure apparatus, and the specimens were heated up to 300 °C within 5 min under 3, 6, and 9 GPa.⁹ The optical absorption spectra of the samples were measured in the wavelength range from 280 to 800 nm with a HITACHI U-3500 spectrophotometer. EPR spectra were measured by a Bruker EMX EPR spectrophotometer. All the measurements were carried out at room temperature.

The present glass codoped with Sn and Cu was transparent and colorless. The long-lasting phosphorescence was observed at 510 nm after the illumination of 254 nm UV light. As can be seen from Fig. 1(a), the phosphorescence band is very broad. In general, a long-lasting phosphorescence phenomenon is considered to occur when trapped electrons or holes in a solid are liberated by incident low-energy photons, and the recombination energies of electrons and holes are then released as phosphorescence. When the sample was illuminated with 254 nm light, an almost symmetric EPR sig-

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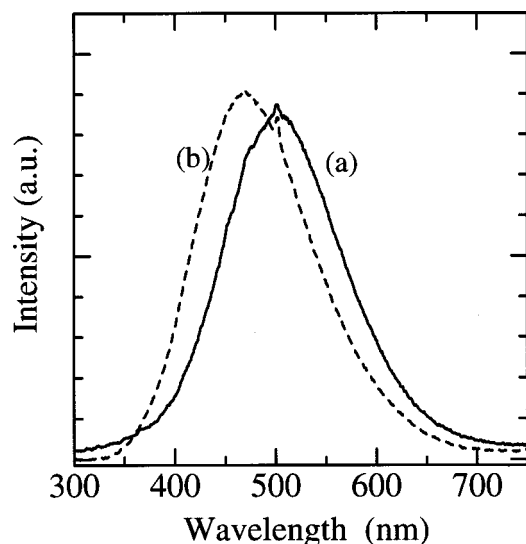


FIG. 1. Phosphorescence spectra of Sn^{2+} - Cu^{2+} codoped Na_2O - CaO - SiO_2 glass under 254 nm UV illumination before (a) and after (b) high-pressure treatment.

nal appeared at $g = 1.999$, as can be seen from Fig. 2(a). This EPR signal is probably due to an electron trapped at the oxygen vacancy site surrounded by Ca^{2+} ions, similar to an F^+ -like center of CaO .¹⁰⁻¹² In the present case, a possible mechanism of the long-lasting phosphorescence can be interpreted as follows. The Sn^{2+} ions act as hole traps, resulting in $\text{Sn}^{2+} + \text{hole} \rightarrow \text{Sn}^{3+}$, where Sn^{3+} is a tin ion of unstable intermediate valency. The free electrons generated by UV illumination were excited from the ground state to the conduction band and then trapped at the oxygen vacancy site surrounded by Ca^{2+} ion. The energy depth of electron trapping site may be shallow and be broadly distributed. It is hence probable that the electrons at the trapping site can be thermally released even at room temperature and recombine with the trapped holes. Thus, the released energies due to the recombination of electrons and holes then transfers to the Cu^{2+} ions. Consequently, a long-lasting phosphorescence phenomenon takes place.

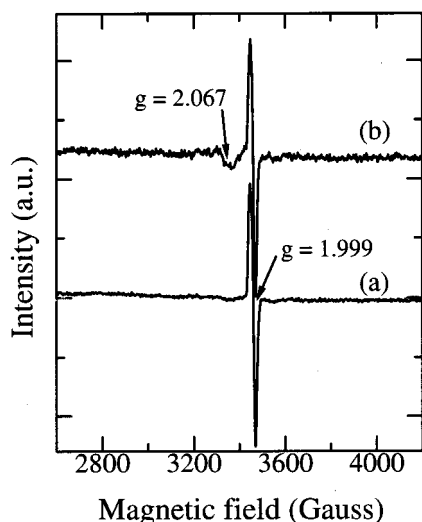


FIG. 2. EPR spectra of Sn^{2+} - Cu^{2+} codoped Na_2O - CaO - SiO_2 glass before (a) and after (b) high-pressure treatment.

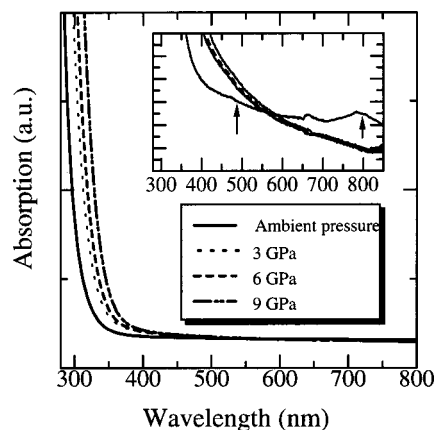


FIG. 3. UV-VIS absorption spectra of Sn^{2+} - Cu^{2+} codoped Na_2O - CaO - SiO_2 glass before and after high-pressure treatment.

As can be seen from Fig. 1(b), it has been found that the phosphorescence peak shifted to a shorter wavelength after compression of the glass. The peak position of 465 nm was independent of the applied pressure. The color of long-lasting phosphorescence is blue green. As shown in the inset of Fig. 3, two absorption peaks at around 450 and 780 nm, which are due to Cu^{2+} , were observed in the optical absorption spectrum of the noncompressed glass samples. These two absorption peaks disappeared in the spectra of the high-pressure treated samples. Therefore, this result indicates that the cupric state, i.e., as Cu^{2+} ions were reduced to cuprous ion, Cu^+ , under a high-pressure condition. The proposed mechanism of the long-lasting phosphorescence mentioned herein can also be applied to compressed samples. In this case, however, blue-green phosphorescence was observed, suggesting the released energy due to recombination of electrons and holes then transferred to the Cu^+ ions.

As shown in Fig. 3, we also found that the optical absorption edge in the UV-visible (UV-VIS) region shifted to lower energies with increasing applied high pressure. In the densification of amorphous SiO_2 and GeS_2 glass similar phenomena have been observed in optical reflection bands.^{4,13} Xu and Ching¹⁴ have investigated the relationship between the optical reflection band and the Si—O bond length,

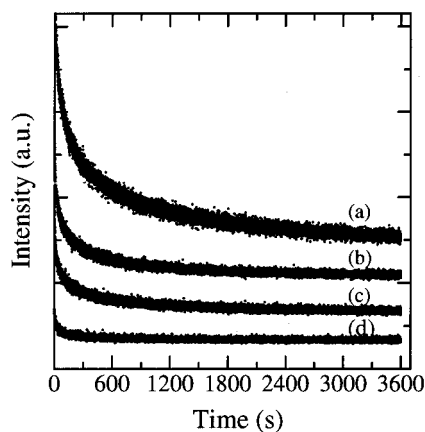


FIG. 4. Decay curves of the long-lasting phosphorescence in Sn^{2+} - Cu^{2+} codoped Na_2O - CaO - SiO_2 glass before (a) and after 3 (b), 6 (c), and 9 (d) GPa treatments. (Decay was monitored at 510 nm for the no high-pressure treated glass and 465 nm for the high-pressure treated glass. The samples were illuminated for 15 min with a 254 nm UV light.

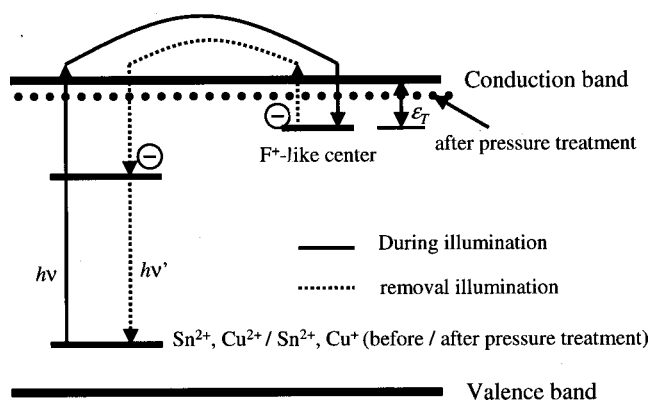


FIG. 5. Tentative model of mechanism for long-lasting phosphorescence in Sn^{2+} - Cu^{2+} codoped Na_2O - CaO - SiO_2 glass before and after high-pressure treatment.

Si-O-Si bond angle and molar volume in several SiO_2 polymorphic forms. They have concluded that there is a correlation among the optical reflection band and the Si-O bond length and molar volume.¹⁴ The decay rate of long-lasting phosphorescence is inversely proportional to the depth of trapping potential ϵ_T . Thus, it is likely that the high-pressure treatment will facilitate the liberation of an electron from its trapping site, since the band gap between the valence band and the conduction band decreased with increasing applied pressure. This consideration was supported by the pressure dependence of the decay rate in Fig. 4. In noncompressed glass, the phosphorescence can be clearly observed by the naked eye even after the elapse of 30 min after cessation of UV light illumination, while in the high-pressure treated glasses, the phosphorescence became faint. In particular, the long-lasting phosphorescence of the glass treated under 9 GPa was hardly observed even immediately after the cessation of the UV light illumination. A possible mechanism of the long-lasting phosphorescence before and after high-pressure treatment is shown in Fig. 5.

In addition, an additional EPR signal around $g=2.067$ was evidently observed after high-pressure treatment, as shown in Fig. 2(b). The EPR signal at $g=1.999$, which is attributed to an F^+ -like center associated with Ca^{2+} ions was induced by illumination UV light, and its intensity greatly changed by the cessation of UV light. The intensity of this additional EPR signal, however, remained unchanged even

after UV light illumination. We therefore suggest that a new hole center is permanently induced by high pressure. Unfortunately, the relationship between the new induced structure and the long-lasting phosphorescence mechanism has not been clarified in the present stage. Further investigation is necessary to make it clear.

In summary, we observed long-lasting phosphorescence in a Sn^{2+} - and Cu^{2+} -doped Na_2O - CaO - SiO_2 glass. We suggest that the long-lasting phosphorescence results from the thermal stimulated recombination of holes and electrons at trapping site induced by UV illumination, which leave holes or electrons in a metastable excited state at room temperature. We also suggest that the change in the optical band gap with the applied high pressure explains the reason why the decay rate of the phosphorescence increases with increasing applied high pressure. We observed that the reduction from cupric ion to cuprous ion by high pressure treatment results in a blueshift of phosphorescence. Furthermore, we observed the appearance of an additional paramagnetic defect after high-pressure treatment. Therefore, we suppose that the appearance of defects may be released by applying other energies, e.g., laser-light illumination. The present phenomena can be used in the fabrication of optical memory devices.

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